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PARTICLE SIZE ANALYSIS OF AMMONIUM SULPHATE AND AMMONIUM PERCHLORATE USING A MALVERN PARTICLE SIZE ANALYSER

L.V. de Yong & H. Fairweather

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Measurement of the particle size of powders is important for many manufacturing operations. In the field of propellants it is also important since the particle size distribution of the ingredients significantly affects not only the burning rate but also the sensitivity of the propellant. This note describes a method used to measure the particle size distribution of ammonium perchlorate and ammonium sulphate, common propellant chemicals, using a low angle light scattering technique.

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Particle size analysis of ammonium sulphate and ammonium perchlorate using a malvern particle size analyser

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ABSTRACT

Measurement of the particle size of powders is important for many manufacturing operations. In the field of propellants it is also important since the particle size distribution of the ingredients significantly affects not only the burning rate but also the sensitivity of the propellant. ~~This note describes~~ a method used to measure the particle size distribution of ammonium perchlorate and ammonium sulphate, common propellant chemicals, using a low angle light scattering techniques is described.

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PARTICLE SIZE ANALYSIS OF AMMONIUM SULPHATE AND AMMONIUM PERCHLORATE USING A MALVERN PARTICLE SIZE ANALYSER

1. INTRODUCTION

The characterization and control of the particle size of powders during their manufacture and processing is often important. The particle size and shape of the ingredients used in explosives and propellants is particularly significant not only in terms of processing, but more importantly in terms of the sensitivity, reactivity and the performance of the end product. For example, the burning rate of a propellant, which is crucial to reliable and accurate operation of a propulsion system, is heavily dependent on the particle size distribution of the ingredients. This note describes the particle size analysis of ammonium perchlorate, a common propellant ingredient, and ammonium sulphate, a common inhibitor in rocket technology, using a Malvern 3600 Particle Size Analyser.

2. PARTICLE SIZING THEORY

The Malvern 3600 uses the Fraunhofer principle (the low angle forward scattering of radiation) to determine the particle size of powders and aerosols dispersed in air or powders dispersed in a liquid medium.

When a particle is illuminated by a parallel beam of monochromatic, coherent light a diffraction pattern is formed. The diffraction angle is inversly proportional to the particle diameter and is represented by the relationship [1]:

$$\theta = \frac{k\lambda}{d} \tag{1}$$

where λ is the wavelength of the incident light
d is the particle diameter
θ is the diffraction angle for the intensity maximum of the diffraction pattern, and
k is a constant.

If a lens is placed in the light beam and a screen placed at the focal length of the lens, the diffracted light forms a pattern of rings around the central point of the screen. This pattern of rings is defined by the relationship [1]:

$$X = \frac{f\lambda}{d} \tag{2}$$

where f is the focal length of the lens, and
X is the distance between successive rings or intensity maxima.

If the screen is replaced by a detector that consists of fifteen photosensitive rings the light energy distribution of the diffraction pattern can be measured. The light energy distribution, due to many particles in the light beam, is mathematically processed to determine the number distribution of the scattering particles then converted to a weight distribution. This assumes the density of the particles is independent of the particle size [1,2].

Because of the difficulties involved in characterizing particle shape, all the particles are assumed to be perfect spheres. Therefore, theoretically, the Malvern 3600 determines the weight distribution of spheres of equivalent diffraction pattern. For most applications, this distribution approximates to the weight distribution of the projected area diameter [3] where the projected area diameter is the diameter of a sphere with an area equal to the projected area of the particle.

3. EXPERIMENTAL VARIABLES

To determine the particle size of a powder dispersed in a liquid using the Malvern 3600, three variables need to be examined: the focussing lens, the liquid for sample dispersion and the assumed particle size distribution function.

The Malvern 3600 can analyse particles in the size range 1.2 µm to 1800 µm. This wide size range is achieved using 6 different focussing lenses, each covering a specific size range. Generally, an initial analysis is carried out using either a 100 mm lens (1.9 µm - 188.0 µm) or a 300 mm lens (5.7 µm - 562 µm) to obtain a rough value of the mean/median particle size.

However, for accurate analysis, the correct lens must be used. The choice of the correct lens is based on the requirement that the measured mean/median particle size lies in the middle of the lens particle size range.

The powdered sample is dispersed in the liquid by placing it in an ultrasonic bath for five minutes and a wetting agent added if needed. The choice of the most appropriate liquid dispersant is determined from visual inspection and the measured value of the particle size. Visually, the sample should disperse well in the liquid and not agglomerate. Also the mean/median particle size should be as low as possible, indicating a well dispersed sample.

In theory, it is possible to obtain the particle size distribution for spherical particles directly from the measured light energy distribution. In practice, problems occur [3]. Alternative methods are therefore used: either a 2 parameter model for the particle size distribution is assumed and fitted to the experimental data in a least squares fit or an iterative heuristic technique is used. The current Malvern software allows three 2 parameter models (Normal, Log-Normal and Rosin Ramler) and one heuristic method (Model Independent).

1. Normal Distribution (N):

This distribution can be represented by:

$$n_d = \frac{1}{N\sqrt{2\pi}} e^{\frac{(d-x)^2}{2N^2}} \tag{3}$$

where n_d is the relative frequency of particles size d, x is the sample mean and N the standard deviation of the distribution. This distribution is appropriate for modelling highly monodisperse samples. It is rarely used in modelling distributions by weight as manufacturing processes characteristically give normal number distributions and thus log normal weight distributions [4]. However, materials showing normal distributions are found among particulate substances produced by chemical processes such as condensation and precipitation [5].

2. Log Normal Distribution (L/N):

The L/N distribution is the logarithmic form of the normal distribution:

$$I_d = \frac{1}{\ell n(N)\sqrt{2\pi}} e^{\frac{(\ell n(d) - \ell n(x))^2}{2\ \ell n(N)^2}} \tag{4}$$

where I_d is the frequency of particles of size d, x is the geometric mean and N is the geometric standard deviation.

This produces a skewed distribution similar to the Rosin Ramler distribution. If a powdered sample has been processed by mechanical means (milling, grinding, etc), the size distribution is very often governed by the L/N law. Consequently, the L/N distribution is the most widely accepted distribution for powders [1,5].

3. Rosin-Ramler Distribution (R/R):

The R/R distribution is given by:

$$R = 100\, e^{(-d/Y)^N} \tag{5}$$

where R is the percentage of the total number of particles which have a diameter greater than d, Y is the peak value of the frequency distribution and N is a measure of the width of the distribution. This distribution was originally developed for modelling crushed coal powders. Its applicability has since extended to cements, clays, ores, sands etc [5]. Recently, it has also been found to be useful in modelling droplet sizes in aerosols [6]. It has been suggested that the use of the R/R distribution should be restricted to samples showing a greater departure from normality than those obeying the L/N distribution and samples obtained by sieving [6].

4. Model Independent (M/I):

If none of the above mathematical functions provide a suitable fit for the size distribution, a Model Independent (M/I) technique may be used. This technique calculates the particle size distribution directly from the observed light intensity without assuming any mathematical relationship for the size distribution. It sets up fifteen size bands (corresponding the the fifteen sensor rings of the detector) and generates a representative diffraction pattern which is compared with the measured diffraction pattern. The advantage of this technique is that all size distributions, including bimodal and trimodal distributions, can be measured [1,2,7].

The correct choice of the lens, dispersant and distribution (which may be determined from prior knowledge of the sample's particle size, solubility in various dispersants etc) is reflected in the magnitude of the log error (L/E) value of the computed mean/median particle size. This L/E value is the logarithm of the sum of the squares of the difference between the measured light energy falling on the detector and the computed light energy based on the assumed distribution function. This error is minimized in an iterative least-squares search and is thus a measure of the fit between the measured and assumed particle size distribution. Consequently, high values of L/E will be recorded for poor choice of distribution, inappropriate lens, poor sample presentation etc. The interpretation of the L/E values is given in Table 1.

4. PARTICLE SIZE ANALYSIS

Analysis was conducted on two samples of ammonium sulphate (A309 & A306) and a single sample of ammonium perchlorate (A229) using the Malvern 3600. The effect of lens size, dispersant and assumed size distribution function on the L/E value and the mean/median particle size were examined to determine the optimum parameters for particle size analysis.

4.1 Ammonium Sulphate

The particle size analysis of ammonium sulphate (A309) dispersed in toluene, chloroform and isopropanol and using a 100 mm lens is shown in Table 2. Both toluene and chloroform give noticeably larger median values than isopropanol. Comparison between the different fitting techniques shows that the L/E values are acceptable for isopropanol and chloroform with M/I, unacceptable for all dispersants using the Normal distribution and acceptable for isopropanol only with L/N and R/R distributions. This suggests isopropanol as the best dispersant and using the M/I and L/N distributions similar median particle sizes are obtained (17 μm and 18.5 μm) .

Verification of this was carried out by sizing a new sample of ammonium sulphate (A306) again with a 100 mm lens and using isopropanol and toluene. Table 3 shows that all the distributions and dispersants give unacceptable L/E values with the exception of isopropanol using M/I and R/R. The median particle size is between 20 μm and 30 μm which suggests a 300 mm lens should have been used and explains the high L/E values.

Results for re-analysing A306 using a 300 mm lens is shown in Table 4. Again, unacceptable L/E values were recorded for both dispersants using the Normal distribution. The R/R and M/I distributions give acceptable L/E values for both dispersants yet the median particle size is lowest for isopropanol. The L/N distribution gives similar median sizes for both dispersants but the L/E value for toluene is unacceptable. These results suggest that isopropanol is the most suitable dispersant with the M/I distribution giving the lowest L/E values.

Ideally, the correct dispersant should give similar values for mean/median particle size regardless of the assumed distribution and the lens used. However, the suitability of distribution and lens will be reflected in the L/E value. Comparison of the data for isopropanol in Tables 3 and 4 shows the median value is approximately independent of the type of distribution and the lens. Comparison of L/E values shows they are lower for the 300 mm lens confirming its suitability over the 100 mm lens. Similarly, the L/E values confirm the suitability of the M/I, R/R and L/N distributions but the M/I distribution gives the lower L/E values.

4.2 Ammonium Perchlorate

Table 5 shows the results of particle size analysis of ammonium perchlorate, A229, dispersed in chloroform, toluene, and petroleum ether and using a 300 mm lens. Isopropanol and water were rejected as dispersants because ammonium perchlorate is soluble in both. Chloroform gives the lowest median particle size for all distributions and toluene gives marginally greater median values. Petroleum ether however gives noticeably larger median values. Comparison between the distributions shows that the L/E values are acceptable for all dispersants with R/R, M/I and L/N distributions but are unacceptable for all dispersants with the Normal distribution. This suggests chloroform is the best dispersant with M/I, L/N and R/R distributions all giving similar median particle sizes (27.5 μm, 28.5 μm and 26 μm respectively) and acceptable L/E values. The M/I distribution however gives the lower L/E value.

Analysis was also conducted with chloroform and toluene and using a 100 mm lens. Table 6 shows that the median particle size with chloroform is similar for all distributions and is in good agreement with the results using the 300 mm lens. Toluene however gives a similar median value with the R/R distribution, but markedly larger values with the other distributions. The L/E values are unacceptable for all dispersants with all distributions excepting Chloroform with M/I. These results confirm the unsuitability of the 100 mm lens and reinforce the choice of chloroform as the most appropriate dispersant with the M/I distribution.

5. CONCLUSIONS

1. Powders dispersed in a liquid can be rapidly sized using the Malvern 3600 Paticle Size Analyser. Care must, however, be taken in the correct choice of dispersant, lens size, and the assumed mathematical distribution.

2. Ammonium sulphate and ammonium perchlorate may be sized by dispersion in isopropanol and chloroform respectively.

3. The Model Independent, Log Normal and Rosin-Ramler distributions generally gave similar mean/median particle sizes and acceptable Log Error values indicating their superiority to the Normal distribution. The Model Independent distribution, however, gave the lowest Log Error values. Note that, this is true for these specific samples of ammonium sulphate and ammonium perchlorate only as the distribution will be dependent on the sample history (manufacture, pre-treatment etc).

6. REFERENCES

1. Weiner, B.B., (1984) "Particle and Droplet Sizing Using Fraunhofer Diffraction" Chapter 5 in Modern Methods of Particle Size Analysis H. G. Bath Ed.) John Wiley & Sons Inc., New York, USA.

2. Malvern Particle Sizer 2600/3600 Manual (1983). Malvern Instruments, Malvern, Worcs., England.

3. Seville, J.P., Coury, J.R., Ghandiri, M. and Clift, R. (1984). "Comparison Techniques for Measuring the Size of Fine Non-Spherical Powders", Part. Charact., 1, 2, 45.

4. Allen, T. (1981). Particle Size Measurement, 3rd Ed., Chapman and Hall, London, p. 136.

5. Herdan, G. (1953). Small Particle Statistics, Elsevier Publishing Company, The Netherlands.

6. Negus, C. and Azzopardi, B.J. (1978). "The Malvern Particle Size Distribution Analyser: Its Accuracy and Limitations", UK Atomic Energy Establishment Report 9075, AERE, Harwell, England.

7. Felton, P.G. (1978). "Instream Measurement of Particle Size Distributions", Symp. on Instream Measurements of Particulate Solids, Bergen, Norway.

TABLE 1

INTERPRETATION OF LOG ERROR VALUES FOR ALL DISTRIBUTIONS

Model	Log Error (L/E)	Comments
Model Independent	LE > 5	Bad fit, systematic errors present
	5 > LE > 4	Adequate fit
	4.5 > LE > 3.5	Good fit, well presented sample
	3.5 > LE	Excellent fit
Normal Log Normal Rosin Ramler	LE > 6	Model not appropriate or experiment performed incorrectly.
	6 > LE > 5.5	Poor fit
	5.5 > LE > 5	Adequate fit, systematic misfitting may be present.
	5 > LE > 4	Good fit, well presented sample
	4 > LE	Excellent fit

TABLE 2

PARTICLE SIZE ANALYSIS OF AMMONIUM SULPHATE A309

USING 100MM LENS

Dispersant	Distribution	Particle Size (μm)		Log Error	N
		Mean	Median		
Toluene	Model Independent	-	78.0	4.9	-
Isopropanol	Model Independent	-	17.0	2.6	-
Chloroform	Model Independent	-	51.5	3.5	-
Toluene	Log Normal	37.81	49.0	6.1	2.9
Isopropanol	Log Normal	18.44	18.5	3.4	2.4
Chloroform	Log Normal	113.45	115.0	6.2	2.9
Toluene	Rosin Ramler	23.24	18.5	6.3	2.2
Isopropanol	Rosin Ramler	17.58	13.5	4.3	1.9
Chloroform	Rosin Ramler	134.01	100.0	5.6	3.5
Toluene	Normal	11.38	-	6.5	5.2
Isopropanol	Normal	4.56	-	6.1	5.9
Chloroform	Normal	42.92	-	6.4	4.9

Note: The N value is a measure of the distribution "spread" as defined in Equations 3,4 & 5.

TABLE 3

PARTICLE SIZE ANALYSIS OF AMMONIUM SULPHATE A306

USING 100 MM LENS

Dispersant	Distribution	Particle Size (µm)		Log Error	N
		Mean	Median		
Toluene	Model Independent	-	65.0	4.9	-
Isopropanol	Model Independent	-	19.5	3.1	-
Toluene	Log Normal	30.3	31.0	5.8	2.4
Isopropanol	Log Normal	33.0	32.5	5.5	2.9
Toluene	Rosin Ramler	24.4	20.5	6.1	2.2
Isopropanol	Rosin Ramler	40.2	30.5	4.3	1.6
Toluene	Normal	14.13	-	6.3	4.6
Isopropanol	Normal	18.18	-	6.2	5.9

Note: The N value is a measure of the distribution "spread" as defined in Equations 3,4 & 5.

TABLE 4

PARTICLE SIZE ANALYSIS OF AMMONIUM SULPHATE

A306 USING 300 MM LENS

Dispersant	Distribution	Particle Size (μm)		Log Error	N
		Mean	Median		
Toluene	Model Independent	-	74.0	2.8	-
Isopropanol	Model Independent	-	29.0	2.9	-
Toluene	Log Normal	30.4	32.0	5.3	3.0
Isopropanol	Log Normal	33.5	34.0	3.9	2.8
Toluene	Rosin Ramler	119.6	76.0	4.4	0.9
Isopropanol	Rosin Ramler	37.2	30.0	3.6	1.4
Toluene	Normal	14.4	-	6.0	4.7
Isopropanol	Normal	17.4	-	6.0	5.7

Note: The N value is a measure of the distribution "spread" as defined in Equations 3,4 & 5.

TABLE 5

PARTICLE SIZE ANALYSIS OF AMMONIUM PERCHLORATE A229

USING 300 MM LENS

Dispersant	Distribution	Particle Size (µm)		Log Error	N
		Mean	Median		
Chloroform	Model Independent	-	27.5	3.1	-
Toluene	Model Independent	-	34.0	2.4	-
Petroleum Ether	Model Independent	-	44.0	3.3	-
Chloroform	Log Normal	29.3	28.5	4.5	2.9
Toluene	Log Normal	38.5	33.5	4.6	2.4
Petroleum Ether	Log Normal	80.4	78.0	4.9	2.9
Chloroform	Rosin-Ramler	36.2	26.0	3.9	1.2
Toluene	Rosin-Ramler	35.2	27.5	5.1	2.0
Petroleum Ether	Rosin-Ramler	76.2	38.0	4.4	1.6
Chloroform	Normal	15.1	-	5.8	4.9
Toluene	Normal	20.6	-	5.9	6.7
Petroluem Ether	Normal	32.5	-	6.4	10.6

Note: The N value is a measure of the distribution "spread" as defined in Equations 3,4 & 5.

TABLE 6

PARTICLE SIZE ANALYSIS OF AMMONIUM PERCHLORATE

A229 USING 100 MM LENS

Dispersant	Distribution	Particle Size (μm)		Log Error	N
		Mean	Median		
Chloroform	Model Independent	-	25.0	3.2	-
Toluene	Model Independent	-	60.0	6.1	-
Chloroform	Log Normal	24.2	24.0	5.3	2.7
Toluene	Log Normal	80.6	76.0	6.1	2.5
Chloroform	Rosin-Ramler	26.8	24.5	5.4	1.7
Toluene	Rosin-Ramler	41.4	22.0	6.2	2.7

Note: The N value is a measure of the distribution "spread" as defined in Equations 3,4 & 5.